SPECIFICATION AMENDMENTS

On page 1, insert above line 1, insert--Priority Claim

The present application claims priority on European Patent Application 02259016.0 filed 30 December 2002.—

On page 1, above line 1, insert--Field of the Invention--

On page 1, above line 14, insert--Background of the Invention--

Paragraph on page 1, line 14, ending on page 2, line 9, has been amended as filed:

-- The preparation of detergents, especially biodegradable detergents, from linear olefins prepared in a Fischer-Tropsch process has been described in the literature. For instance, in ACS Symp. Series No. 238, 18-33 (191 ACS Nat. Meeting Div. Pet. Chem. Symp. New York, 13-18 April 1986) it has been described that Co-C15 cuts of low and high temperature Fischer-Tropsch processes are suitable feedstocks in the alkylation of benzene to prepare alkylbenzenes, followed by sulfonation to convert the alkylbenzenes into alkylbenzenesulphonates sulfonates. The direct products of these Fischer-Tropsch processes, using iron based catalysts, comprise rather large amounts of olefins and oxygenates (usually alcohols). For instance, the high temperature process results in a product comprising about 70% olefins (60% straight chain product), the low temperature process results in about 25% olefins (linearity 93%). Also, U.S. Pat No.3,674,885 describes the use of paraffin-olefin mixtures synthesized in a Fischer-Tropsch process in the alkylation of benzene. The paraffins are separated from the alkylation mixture and are recycled to a chlorination unit from which the paraffin-chloroparaffin effluent mixture is combined with the fresh Fischer-Tropsch olefin-paraffin mixture and the combined feeds are used to alkylate the benzene. --

Paragraph on page 2, at line 10, has been amended as follows:

-- In the prior art processes, however, the separation and the use of the available detergent hydrocarbons is not optimal. Further, the presence of unsaturated compounds

make storage and transport difficult. Additionally, the The use of a chlorination process is undesirable not desired.

On page 2, after line 14, insert-- Summary of the Invention

The present invention is directed to a process for the preparation of detergents, comprising separating the hydrocarbonaceous product stream from a Fischer-Tropsch process producing normally liquid and normally solid hydrocarbons into a light fraction comprising mainly C₂₀-hydrocarbons, preferably at least 90 %wt, more preferably at least 95 %wt, of C₂₀-hydrocarbons, and one or more heavy fractions comprising the remaining hydrocarbons, hydrogenating at least part of the light fraction to convert unsaturated hydrocarbons and/or oxygenates into saturated hydrocarbons, distilling product thus obtained into at least one fraction comprising detergent hydrocarbons, dehydrogenating at least part of the detergent hydrocarbons to obtain a detergent hydrocarbon stream comprising mono-olefins and converting the mono-olefins into detergents.

In another embodiment, the invention is directed to a process for the preparation of detergents in which process a hydrogenated product, which product is obtained by separating the hydrocarbonaceous product stream from a Fischer-Tropsch process producing normally liquid and normally solid hydrocarbons into a light fraction comprising mainly C₂₀-hydrocarbons, preferably comprising at least 90 %wt, more preferably at least 95 %wt, of C₂₀-hydrocarbons, and one or more heavy fractions comprising the remaining hydrocarbons, hydrogenating at least part of the light fraction to convert unsaturated hydrocarbons and/or oxygenates into saturated hydrocarbons and distilling product thus obtained into at least one fraction comprising detergent hydrocarbons, is dehydrogenated to obtain a detergent hydrocarbon stream comprising mono-olefins, followed by conversion of the mono-olefins into detergents.--

On page 2, above line 15, insert--Detailed Description of the Invention--

In this specification the term "mainly" means at least 80 %wt, unless otherwise specified. When an amount of a product or mixture is indicated as "%wt", the percentage is based on the total product stream in which the product is present, unless otherwise specified. By "normally liquid hydrocarbon product" is meant any product which is at STP (1 bar, 0 °C) a liquid product. For saturated hydrocarbons this means C₅₊ hydrocarbons.

By "normally solid product" is meant any product which is solid at STP. For saturated normal hydrocarbons this means C_{15+} . The term C_{n+} relates to molecules comprising n carbon atoms or more. The term C_{n-} refers to molecules comprising n carbon atoms or less. The term "middle distillates", as used herein, is a reference to hydrocarbon mixtures of which the boiling point range corresponds substantially to that of kerosene and diesel fractions obtained in a conventional atmospheric distillation of crude mineral oil.--

Paragraph on page 2, line 15, ending on page 3, line 12, has been amended as follows: -- It is now proposed to isolate The present invention involves isolating a particular fraction from a Fischer-Tropsch product, followed by hydrogenation and distillation to obtain the desired detergent hydrocarbons (i.e. hydrocarbons to be used for the preparation of detergents, often C₁₀-C₁₃ and/or C₁₄-C₁₇ linear paraffins), followed by [[(]]catalytical[[)]] dehydrogenation to obtain a detergent hydrocarbon stream comprising mono-olefins and converting the mono-olefins into detergents using processes known in the art, these processes usually resulting in a mixture comprising between 5 and 20% monoolefins. The proposed scheme has the advantage that very narrow production ranges can be obtained, as the distillation of hydrogenated product results in a more uniform carbon distribution pattern than a raw Fischer-Tropsch product comprising olefins and oxygenates (mainly alcohols). In addition, an optimum yield is obtained as none of the molecules having the desired number of carbon atoms ends up in the lower or higher boiling fraction. This is an important aspect, as, due to the tendency to maximise maximize the carbon chain length of the products in the Fischer-Tropsch process, the amount of relatively low boiling compounds becomes less and less. Thus, an optimum use of the relatively low boiling products is desired. Further, such hydrogenated products are more stable and less corrosive than non-treated products, making transport and storage easier more easy. In addition, the use of only a light fraction of the raw Fischer-Tropsch products avoids the need to hydrogenate the full Fischer-Tropsch fraction, as it is often not necessary to hydrogenate the heavy Fischer-Tropsch product. --

On page 3, delete line 13-33.

On page 4, delete line 1-13.

Paragraph on page 4, line 14, ending on page 5, line 2, has been amended as follows:

-- In the above processes, for reasons of efficiency, the The light Fischer-Tropsch fraction suitably comprises at least 80 %wt (on total fraction) of C₂₀-products. Preferably the light fraction comprises 90 %wt, more preferably 95 %wt, C₁₈-hydrocarbons, especially at least 80 %wt, preferably 90 %wt, more preferably 95 %wt, C₁₆-hydrocarbons, more especially at least 80 %wt, preferably 90 %wt, more preferably 95 %wt, C₁₄-hydrocarbons. The light fraction comprises for a large part saturated paraffins, together with olefins and oxygenates. The oxygenates are mainly alcohols. The carbon skeleton of the paraffins, olefins and alcohols are identical, and usually contain between 2 and 20 %wt, more usually between 4 and 14 %wt, of branched carbon chains. The amount of branched structures depends on the actual process conditions (especially pressure, temperature, H₂/CO ratio, catalyst, catalyst activators). Methyl groups, usually present in up to 15% of the molecules based on total molecules, more usually in up to 10%, are the main form of branches present.--

Paragraph on page 5, line 3, has been amended as follows:

-- Very suitably, the hydrocarbonaceous product stream of the Fischer-Tropsch process, before separation into the light fraction and the heavy fraction, is separated into a light stream, comprising most, suitably at least 80 %wt, preferably 90 %wt, more preferably 95 %wt, of the C₁-C₄ hydrocarbons produced in the Fischer-Tropsch process, especially the light product stream comprising most, suitably at least 80 %wt, preferably 90 %wt, more preferably 95 %wt, of the C₁-C₃ hydrocarbons produced in the Fischer-Tropsch process, and optionally unconverted synthesis gas constituents, carbon dioxide and other inert gases, and a heavy stream which is separated into the light and the heavy fraction. If still present, also Fischer-Tropsch process water is also removed. In another embodiment the Fischer-Tropsch product stream is first separated into a light and a heavy fraction, followed by removal of the above described light stream.--

Paragraph on page 5, line 20, ending on page 6, line 2, has been amended as follows:

-- In a further preferred embodiment, for reasons of efficiency, also a light product is removed from the hydrocarbonaceous product stream from the Fischer-Tropsch process or the light stream as described above, the light product stream comprising

eontaining mainly, especially at least 80 %wt, the C₇-products, preferably the C₈-products, more preferably the C₉-products, present in the stream, especially the light product comprising at least 90 %wt, more preferably at least 95 %wt, of the C₇-products present, more especially the light product comprising at least 90 %wt, preferably at least 95 %wt, of the C₈-products present, still more especially the light product comprising at least 90 %wt, more preferably at least 95 %wt, of the C₉-products present.

Paragraph on page 6, line 3, has been amended as follows:

-- In a preferred embodiment, resulting in an the most optimal and efficient use of the detergent hydrocarbons, the light fraction which is to be hydrogenated comprises mainly C9- to C18-hydrocarbons, preferably at least 80 %wt C9- to C18-hydrocarbons, more preferably at least 90 %wt, especially the light fraction comprising mainly C10- to C14-hydrocarbons, preferably at least 80 %wt C10 to C13-hydrocarbons, more preferably at least 90 %wt. In another preferred embodiment, the light fraction which is to be hydrogenated comprises al least 80 %wt C14- to C18-hydrocarbons, preferably at least 90 %wt, especially at least 80 %wt C14- to C17-hydrocarbons, preferably at least 90 %wt. In the above preferred embodiment, the distillation of the hydrogenated hydrocarbons is not always necessary, and thus is an optimal feature. The boiling range is suitably between 160 °C and 330 °C, preferably between 170 °C and 320 °C. Especially preferred are the ranges between 170 °C and 240 °C and between 250 °C and 310 °C.--

Paragraph on page 6, line 22, ending on page 7, line 5, has been amended as follows:

-- The Fischer-Tropsch process is suitably a low temperature process. In the Fischer-Tropsch process a mixture of hydrogen and carbon monoxide is catalytically converted into hydrocarbons and water. The Fischer-Tropsch catalysts are known in the art. Catalysts for use in this process frequently comprise, as the catalytically active component, a metal from Group VIII of the Periodic Table of Elements. Particular catalytically active metals include ruthenium, iron, cobalt and nickel. Cobalt is a preferred catalytically active metal in view of the heavy Fischer-Tropsch hydrocarbon which can be made. Preferred hydrocarbonaceous feeds are natural gas or associated gas. As these feedstocks usually

result results in synthesis gas having H_2/CO ratio's of about 2, cobalt is a very good Fischer-Tropsch catalyst as the user ratio for this type of catalysts is also about 2.

Paragraph on page 8, line 20, ending on page 9, line 14, has been amended as follows:

-- The catalytic conversion process may be performed under conventional synthesis conditions known in the art. Typically, the catalytic conversion may be effected at a temperature in the range of from 180 to 270 °C, preferably from 200 to 250 °C. Typical total pressures for the catalytic conversion process are in the range of from 10 to 100 bar absolute, more preferably from 20 to 65 bar absolute. In the catalytic conversion process preferably especially more than 75 %wt of C₅₊, and more preferably more than 85 %wt C₅₊ hydrocarbons are formed. Depending on the catalyst and the conversion conditions, the amount of heavy wax (C20+) may be up to 60 %wt, sometimes up to 70 %wt, and sometimes up to even up till 85 %wt. Preferably a cobalt catalyst is used, a low H₂/CO ratio is used (especially 1.7, or even lower) and a low temperature is used (190-240 °C), optionally in combination with a high pressure. To avoid any coke formation, it is preferred to use an H₂/CO ratio of at least 0.3. It is especially preferred to carry out the Fischer-Tropsch reaction under such conditions that the ASF-alpha value (Anderson-Schulz-Flory chain growth factor), for the obtained products having at least 20 carbon atoms, is at least 0.925, preferably at least 0.935, more preferably at least 0.945, even more preferably at least 0.955. Preferably the Fischer-Tropsch hydrocarbons stream comprises at least 40 %wt C_{30+} , preferably 50 %wt, more preferably 55 %wt, and the weight ratio C_{60+}/C_{30+} is at least 0.35, preferably 0.45, more preferably 0.55.-

Paragraph on page 11, line 21, ending on page 12, line 7, has been amended as follows:

--The hydrogenation step is operated under conditions such that substantially no isomerisation isomerization or hydrocracking of the feed occurs. The precise operating conditions required to achieve the desired degree of hydrogenation without substantial hydrocracking or hydroisomerisation hydroisomerization occurring will vary according to the composition of the hydrocarbon product being fed to the hydroconversion stage and the particular catalyst being employed. As a measure of the severity of the conditions prevailing in the first hydroconversion stage and, hence, the degree of hydrocracking and isomerisation isomerization occurring, the degree of conversion of the feed hydrocarbon may be

determined. In this respect, conversion, in percent, is defined as the percent weight of the fraction of the feed boiling above 220 °C which is converted during the hydroconversion to a fraction boiling below 220 °C. The conversion of the first hydroconversion stage is below 20%, preferably below 10%, more preferably below 5%. In the case that there is too much hydroisomerisation hydroisomerization and/or hydrocracking a decrease of the temperature may will-resolve the problem.--

Paragraph on page 12, line 8, has been amended as follows:

-- After the hydrogenation step the resulting product is distilled in such a way that the desired detergent hydrocarbons are obtained. Commercially available equipment ean may be used. The distillation may be carried out at atmospheric pressure, but also reduced pressure may also be used.—

Paragraph on page 12, line 19, has been amended as follows:

-- In general, dehydrogenation of the detergent hydrocarbons in the instant process ean may be accomplished using any of the well-known dehydrogenation catalyst systems or "conventional dehydrogenation catalysts" including those described in "Detergent Manufacture Including Zeolite Builders and Other New Materials", Ed. Sittig, Noyes Data Corp., New Jersey, 1979 and other dehydrogenation catalyst systems, for example those commercially available though UOP Corp. Dehydrogenation ean may be conducted in the presence of hydrogen gas and commonly a precious metal catalyst is present though alternatively non-hydrogen, precious-metal free dehydrogenation systems such as a zeolite/air system can may be used with no precious metals present. --

Paragraph on page 13, line 1, has been amended as follows:

-- As is well known, dehydrogenation can Dehydrogenation may be complete or partial, more typically partial. Usually between 5 and 50 %wt olefins are formed, suitably between 5 and 20 %wt. When partial, this step forms a mixture of olefin and unreacted paraffin. Such mixture is may be a suitable feed for e.g. a benzene alkylation step. After work up of the an alkylation step, the unconverted paraffins may be recirculated to the start of the dehydrogenation process.--

Paragraph on page 13, line 19, ending on page 20, line 3, has been amended as follows:

- -- Following the dehydrogenation, the detergent hydrocarbon is converted into a detergent according to methods well known in the art. Suitably, the reaction is selected from the following reactions:
- alkylation with benzene or toluene optionally followed by sulfonation and neutralization neutralisation;
- alkylation with phenol followed by at least one of alkoxylation, sulfonation and <u>neutralization</u> neutralisation, sulfation and <u>neutralization</u> or alkoxylation combined with oxidation;
- hydroformylation optionally followed by at least one of alkoxylation, glycosylation, sulfation, phosphatization phosphatation or combinations thereof
- sulfonation;
- epoxidation;
- hydrobromination followed by amination and oxidation to amine oxide; and
- phosphonation.

Paragraph on page 14, line 4, has been amended as follows:

-- A particularly preferred option is the alkylation of mono-aromatic compounds, e.g. benzene, toluene, xylene and mixtures thereof, followed by sulfonation sulphonation. The alkylation process may use aluminium chloride, HF hydrogen fluoride, fluoridated zeolites, non-acidic calcium mordenite and the like as catalyst. For example, appropriate process conditions for ALC13 alkylation are exemplified by a reaction of 5 mole% ALC13 relative to the detergent hydrocarbon at 100-300 °C for 0.5-1.0 hour in a batch or continuous reactor. Other suitable alkylation catalyst may be selected from shape-selective moderately acidic alkylation catalysts, preferably zeolitic. The zeolite in such catalysts for the alkylation step is preferably selected from the group consisting of mordenite, ZSM-4, ZSM-12, ZSM-20, offretite, gmelinite and zeolite beta in at least partially acidic form. More preferably, the zeolite in the alkylation step is substantially in acid form and is contained in a catalyst pellet comprising a conventional binder and further wherein said catalyst pellet comprises at least about 1%, more preferably at least 5%, more typically from 50% to about 90%, of said zeolite. --

Paragraph on page 14, line 26, has been amended as follows:

-- More generally, <u>a</u> suitable alkylation catalyst is typically at least partially crystalline, more preferably substantially crystalline not including binders or other materials used to form catalyst pellets, aggregates or composites. Moreover, the catalyst is typically at least partially acidic. H-form mordenite is <u>an example of</u> a suitable catalyst. --

Paragraph on page 15, line 1, has been amended as follows:

-- The pores characterizing the zeolites useful in the present alkylation process may be substantially circular, such as in canchinite which has uniform pores of about 6.2 angstroms. Angstroms, or preferably may be somewhat elliptical, such as in mordenite. It should be understood that, in any case, the The zeolites used as catalysts in the alkylation step of the present process may have a major pore dimension intermediate between that of the large pore zeolites, such as the X and Y zeolites, and the relatively small pore size zeolites ZSM-5 and ZSM-11, and preferably between about 6A-6 Angstroms and about 7A 7 Angstroms. The pore size dimensions and crystal structures of certain zeolites are specified in ATLAS OF ZEOLITE STRUCTURE TYPES by W. M. Meier and D. H. Olson, published by the Structure Commission of the International Zeolite Association (1978 and more recent editions). The zeolites may be subjected to various chemical treatments, including alumina extraction (dealumination) and combination with one or more metal components, particularly the metals of Groups IIB, III, IV, VI, VII and VIII. It is also contemplated that the zeolites may, in some instances, desirably be subjected to thermal treatment, including steaming or calcination in air, hydrogen or an inert gas, e.g. nitrogen or helium. In practicing the desired alkylation step of the instant process, it may be useful to incorporate the above-described intermediate pore size crystalline zeolites in another material, e.g., a binder or matrix resistant to the temperature and other conditions employed in the process. Such matrix materials include synthetic or naturally occurring substances as well as inorganic materials such as clay, silica, and/or metal oxides. Matrix materials may ean be in the form of gels including mixtures of silica and metal oxides.--

Paragraph on page 16, line 1, has been amended as follows:

-- The process of the invention is also directed further relates to a process for the preparation of detergents and hydrocarbon fuels from the product stream of a Fischer-Tropsch process, comprising a process as described above for the preparation of

detergents from a light fraction of the Fischer-Tropsch process in combination with the hydrocracking/hydroisomerisation hydroisomerization of the one or more heavy fractions of the Fischer-Tropsch process.—

Paragraph on page 16, line 9, has been amended as follows:

-- In the hydrocracking/hydroisomerisation hydroisomerization step, hydrocarbon fuels are prepared from the hydrocarbon product of the one or more heavy FTT Fischer-Tropsch fractions by hydrocracking and hydroisomerising hydroisomerizing the product with hydrogen in the presence of a suitable catalyst. Typically, the catalyst comprises as catalytically active component one or more metals selected from Groups VIB and VIII of the Periodic Table of Elements, in particular one or more metals selected from molybdenum, tungsten, cobalt, nickel, ruthenium, iridium, osmium, platinum and palladium. Preferably, the catalyst comprises one or more metals selected from nickel, platinum and palladium as the catalytically active component. Catalysts comprising platinum as the catalytically active component have been found to be particularly suitable for use in the second hydroconversion stage.--

Paragraph on page 17, line 15, has been amended as follows:

-- Suitable catalysts for use in the hydrocracking/
hydroisomerisation hydroisomerization stage of the process of this invention are available
commercially, or may be prepared by methods well known in the art, for example the
methods discussed hereinbefore with reference to the preparation of the hydrocarbon
synthesis catalyst.--

Paragraph on page 17, line 21, ending on page 18, line 2, has been amended as follows:

-- In the hydrocracking/hydroisomerisation hydroisomerization stage of this process, the heavy Fischer-Tropsch hydrocarbon product is contacted with hydrogen in the presence of the catalyst at elevated temperature and pressure. Typically, the temperatures necessary to yield the hydrocarbon fuels will lie in the range of from 200 to 400 °C, preferably from 275 to 375 °C. The pressure typically applied ranges from 20 to 250 bars, more preferably from 40 to 200 bars. Hydrogen may be supplied at a gas hourly space velocity of from 100 to 10000 Nl/l/hr, preferably from 500 to 5000 Nl/l/hr. The hydrocarbon feed may be provided at a weight hourly space velocity of from 0.1 to 5

kg/l/hr, preferably from 0.25 to 2 kg/l/hr. The ratio of hydrogen to hydrocarbon feed may range from 100 to 5000 Nl/kg and is preferably from 250 to 2500 Nl/kg.--

Paragraph on page 18, line 3, has been amended as follows:

-- As discussed hereinbefore, the degree of hydrocracking and isomerisation occurring in the hydrocracking/-hydroisomerisation hydroisomerization stage may be measured by determining the degree of conversion of the fraction boiling above 370 °C. Typically, the hydrocracking/-hydroisomerisation hydroisomerization stage is operated at a conversion of at least 40%.--

Paragraph on page 18, line 14, has been amended as follows:

-- The hydrocarbon fuel produced in the second hydroconversion stage will typically comprise hydrocarbons having boiling points lying in a number of <u>ranges for</u> different fuel fractions, for example naphtha, kerosene and gasoil fractions. Separation of the hydrocarbon fuel into the appropriate fractions may be conveniently achieved using distillation techniques well known in the art.--

Paragraph on page 18, line 26, ending on page 19, line 18, has been amended as follows:

-- The present invention <u>is</u> further <u>relates</u> <u>directed</u> to a process for the preparation of detergent hydrocarbons comprising separating the hydrocarbonaceous product stream of a Fischer-Tropsch process producing normally liquid and normally solid hydrocarbons into a light fraction comprising mainly C₂₀-hydrocarbons, preferably C₁₈-, more preferably C₁₆-, still more preferably C₁₄-hydrocarbons, and one or more heavy fractions comprising the remaining hydrocarbons, hydrogenation of the light fraction to convert unsaturated hydrocarbons and/or oxygenates into saturated hydrocarbons, distillation of product thus obtained into at least one fraction comprising detergent hydrocarbons and optionally dehydrogenation of at least part of the detergent hydrocarbons to obtain a detergent hydrocarbon stream comprising mono-olefins. Preferably the process comprises the use of any one or more reject streams, e.g. obtained in the distillation processes, in the process for the preparation of detergent hydrocarbons as additional feedstreams in the process for the preparation of fuels. Further preferred embodiments correspond with the preferred embodiments described in the claims and description for the

process as described in claim 1. A preferred range of C₁₄-C₁₇ detergent hydrocarbons may be converted into detergents via chlorination or sulfonation of the hydrogenated C₁₄-C₁₇ stream.--

Paragraph on page 19, line 19, has been amended as follows:

-- The invention is further relates-directed to a process for the preparation of detergent hydrocarbons and hydrocarbon fuels from the product stream of a Fischer-Tropsch process, comprising a process as described above for the preparation of detergent hydrocarbons from a light fraction of the Fischer-Tropsch process in combination with the hydrocracking/hydroisomerisation hydroisomerization of the heavy product stream of the Fischer-Tropsch process. —

Paragraph on page 19, line 27, ending on page 20, line 10, has been amended as follows.

-- The invention is further relates directed to a process for the preparation of detergents comprising dehydrogenation of detergent hydrocarbons to obtain a detergent hydrocarbon stream comprising mono-olefins and conversion of the mono-olefins into detergents, the detergent hydrocarbons being prepared by separating the product stream of a Fischer-Tropsch process into a light fraction comprising mainly C₂₀-hydrocarbons, preferably C₁₈-, more preferably C₁₆-, still more preferably C₁₄-hydrocarbons, and a heavy fraction comprising the remaining hydrocarbons, hydrogenation of the light fraction to convert unsaturated hydrocarbons and/or oxygenates into saturated hydrocarbons, distillation of product thus obtained into at least one fraction comprising detergent hydrocarbons. Preferred embodiments correspond with the preferred embodiments described in the claims and description for the process as described in claim 1. —

On page 20, delete line 11-28.

On page 21, above line 1, insert -- We claim: --